2004 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Annual Program Review

Development of Supports and Membranes for Hydrogen Separation

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May 24-27, 2004, Philadelphia, PA

Project Objectives

- To develop porous metal supports for hydrogen separation membranes that are compatible with the supported membrane and operational environment
  - develop a flexible fabrication process

- To develop thermodynamically stable, high temperature, high proton flux proton transport membranes (PTM) using a *computational combinatorial chemistry approach*.
  - expand the computational model under development at ORNL that will allow the materials properties to be predicted based on the electronic properties of the elements of the periodic table.

Budget

Project	FY 2004 Budget (k$)
Support Tube Development	100
Proton Transport Membranes	100
Total	200

Technical Targets

- DOE Technical Barriers
  - A. Fuel Processor Capital Costs
  - B. Operation and Maintenance Costs
  - AB. Hydrogen Separation and Purification
- DOE Technical Targets for 2010
  - Purification: 90%at $0.03/kg Hydrogen
  - Palladium Membranes: <$100/ft^2 capable of operating at 300-600 °C for 100,000 hrs with at flux of 200 scfh/ft^2

Technical Approach

Develop a composite support tube structure especially for palladium membranes

- Approach for Porous Support Tube Development
  - Establish performance criteria for support tubes for palladium, microporous, ion-transport membranes
  - Identify potential support tube materials and down select through a rigorous investigation of potential for fabrication and compatibility with Pd (initially)
  - Establish fabrication protocols

- Approach for Proton Transport Membrane Development
  - Atomistic computer simulations are being developed to identify and evaluate potential new proton conducting ceramic systems
  - Rapid high-purity materials synthesis using a modified "combustion synthesis" process
  - Structure and properties (hydrogen flux) characterization
  - Long-term stability testing

Project Safety

- Project has undergone "Integrated Safety Management Pre-Planning and Work Control" (Research Hazard Analysis and Control)
  - Definition of task
  - Identification of hazards
  - Design of work controls
  - Conduct of work
  - Feedback
- Each work process is authorized on the basis of a Research Safety Summary (RSS) reviewed by ESH subject matter experts and approved by PI's and cognizant managers
- The RSS is reviewed/revised yearly, or sooner if a change in the work results in a need for modification.
- Experienced Subject Matter Experts are required for all Work Control for Hydrogen R&D including
- Periodic safety reviews of installed systems

Project Timeline

(Project initiated February 2004)

Support Tube Development

2004-2005	2006-2007
Phase I	**Phase II**

1 2 3 4 5

- Phase I: Development and Testing
  - 1 – Prototype Support Tube
  - 2 – Complete tests to determine efficacy of tubes to accommodate membrane layer(s)
- Phase II: Optimization, Scale up and Tech Transfer
  - 3 – Composite Support Development (initiate)
  - 4 – Complete tests to determine efficacy of composite tubes to accommodate membrane layer(s)
  - 5 – Complete scale up and transition to industry

Project Timeline

(Project initiated February 2004)

Proton Transport Membrane Development

2004-2005	2005-06	2007
Phase I	**Phase II**	**Phase III**

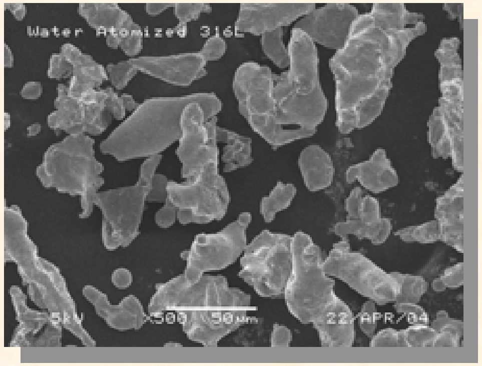
1   2, 3, 4   5 6   7   8

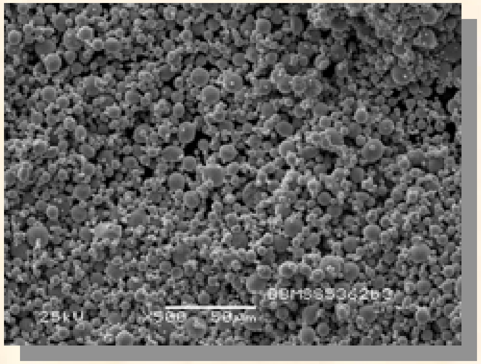
- Phase I: Proof-of-concept
  - 1 – Complete tests to determine viability of Pyrochlore/Perovskite materials (go/no go)
  - 2 – Complete tests to determine viability of novel low-temperature material (go/no go)
  - 3 – Complete tests to determine viability of fluorite proton conductors (go/no go)
  - 4 – Down select to one structural family
- Development and Testing
  - 5 – Optimize flux, composition, and mechanical properties
  - 6 – Asymmetric membrane development on metallic supports
  - 7 – Complete optimization of asymmetric membranes
- Phase II: Optimization, Scale up and Tech Transfer
  - 8 – Complete scale up and transition to industry

Technical Progress
(Porous Support Tube Development)

- Potential support tube materials have been identified and include:
  - 300 and 400 series stainless steels,
  - Iron Aluminide, and
  - Hastelloy X
- Gas (argon or helium) atomized powders have greatest potential for hydrogen membrane supports (powders are spherical and size distribution can be controlled)
- Support tube forming process parameters are being established

Water Atomized



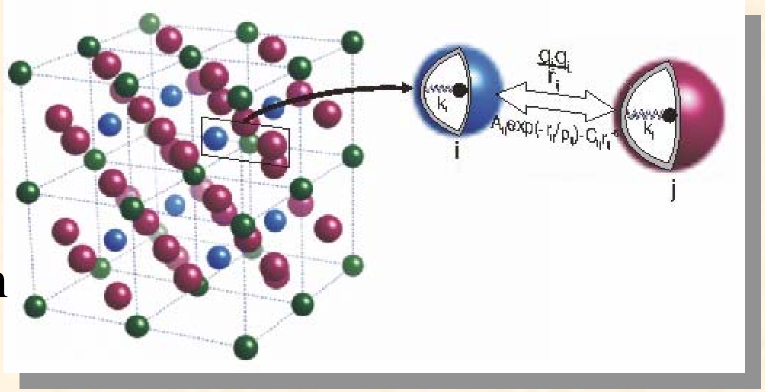


Gas Atomized

Technical Progress
(Proton Transport Membrane Development)

- Potential proton transport materials have been identified in the pyrochlore, brownmillerite, and fluorite families
- Computer simulation with empirical potential models
  - model completed for several pyrochlore, perovskite, and brownmillerite end members. Solid solution and defect models are in development.

- Crystal structure and phase identification studies completed for >100 samples prepared to date with more in progress
- High temperature conductivity measurements in air completed for >30 samples to date - repeat studies in hydrogen are in progress
- Hydrogen permeance measurements are scheduled to begin by May 2004

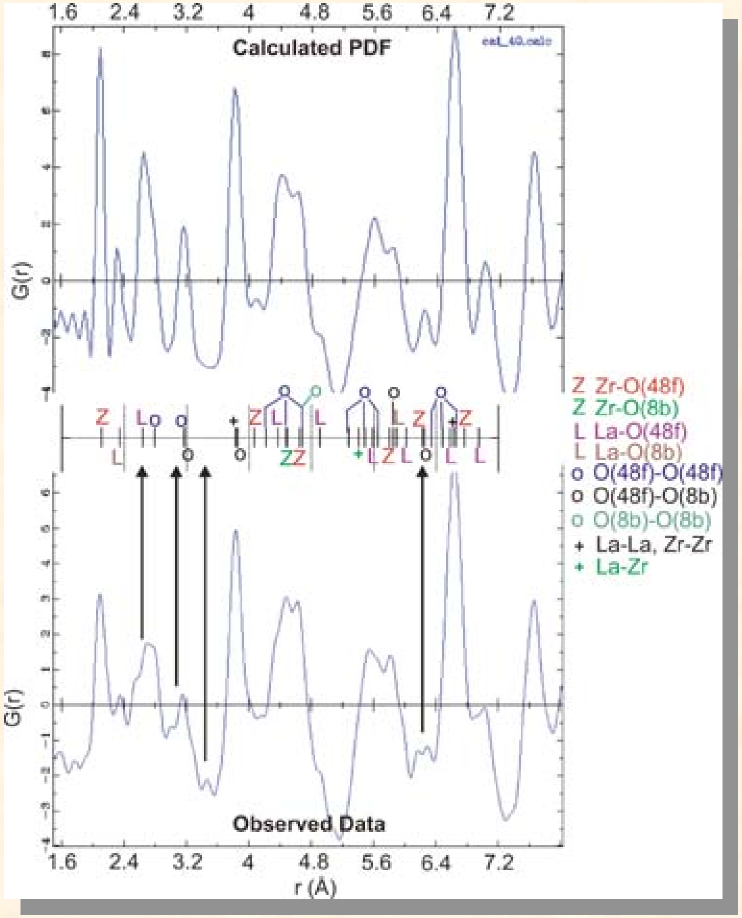


Phase Stability can be Predicted Using Calculated Lattice Energies

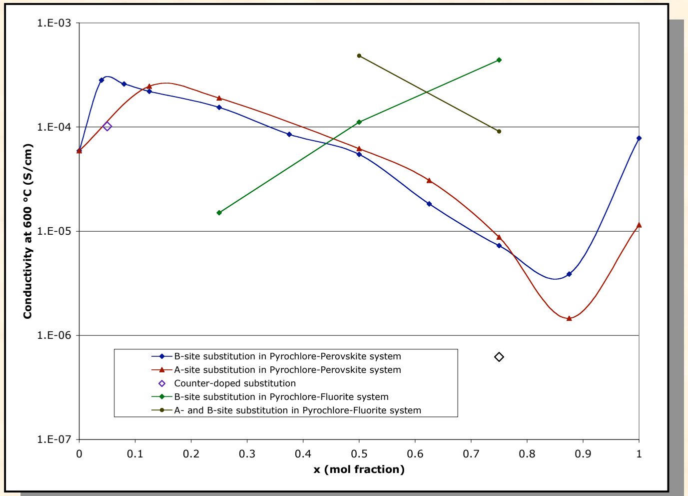
- **The substitution of the dopants Y, Sc, In, Sm, and Ga for the A and B sites in $La_2Zr_2O_7$ were evaluated.**
  - **Y, Ga, Sc, and In were all predicted to dissolve into the pyrochlore structure.**
    - **The dopants preferred to occupy the A sites.**
    - **Ga had the smallest energy differential between A and B site occupancy, while Y had the greatest.**
  - **Y could be substituted onto the B-site in place of Zr at low levels.**
    - **For a composition $La_2Zr_{2-x}Y_xO_{7-x/2}$, A site substitution would produce a La_2O_3 secondary phase. This would produce a greater total energy than is created by B site substitution; therefore, the Y occupies the B site up to a certain level.**
    - **This was observed experimentally, where Y occupied the B site up to x=0.2. Above x=0.2, Y occupied the A site, producing a La_2O_3 secondary phase.**
  - **Sc was predicted to dissolve into the $La_2Zr_2O_7$ pyrochlore. However, it instead formed a mixture of $La_2Zr_2O_7$ and $LaScO_3$.**
    - **The $LaScO_3$ perovskite was not considered in the energetic calculations, and therefore its stability was not predicted.**
    - **New methodologies are being developed to evaluate a broader range of possible products to improve the accuracy of the models predictions.**

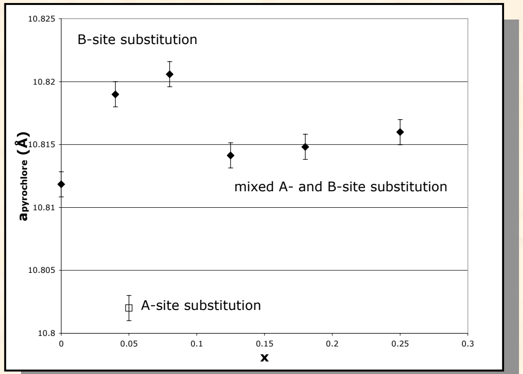
Neutron Scattering Being Used to Correlate Structure Changes to Conductivity

- Neutron scattering is being used to probe the structural subtleties in the doped pyrochlore phases.
- Both diffraction and pair distribution analysis are being used.
- Pair distribution analysis reveals some small differences between in the local order of B site coordination with Y substitution.
- These changes vary based upon the amount of Y substitution.

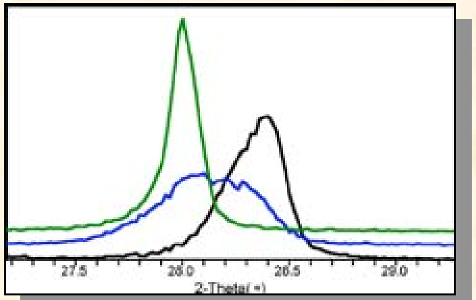


A- and B-site Substitutions Across Pyrochlore-Perovskite System





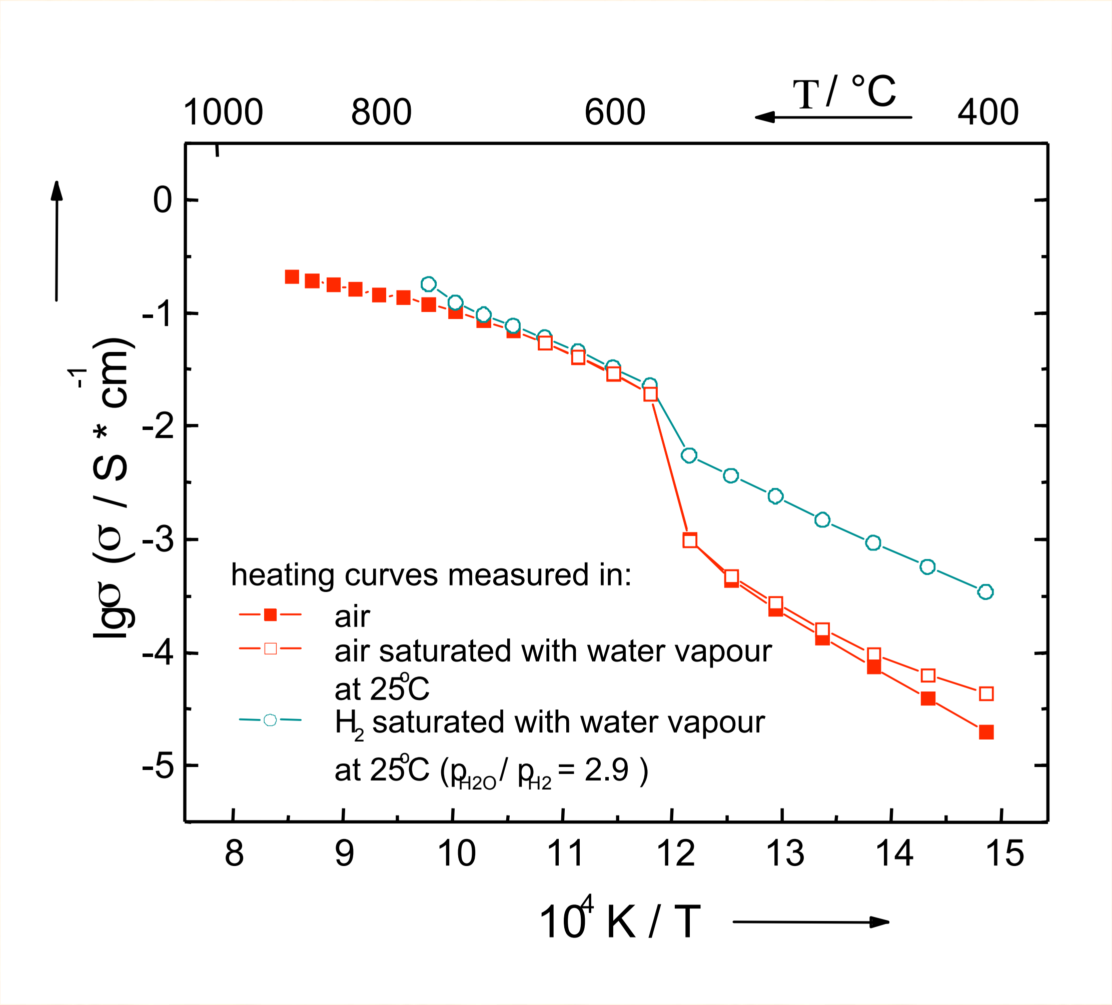
Combined neutron and X-ray explains effects of different site occupation.

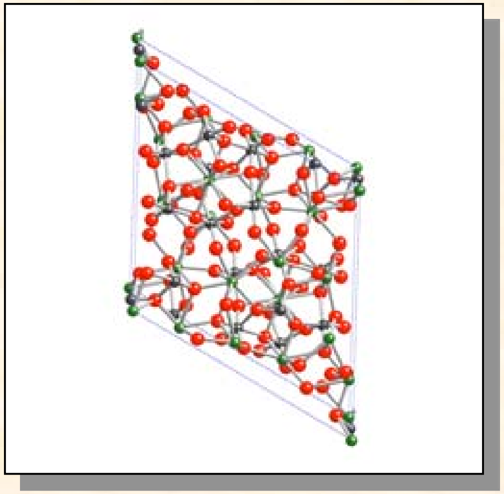


The level of substitution and disorder in the pyrochlore-fluorite system offers promise.

- A- and B-site substitutions produce similar conductivity trends
- The greater B-site dopant solubility in pyrochlore is more effective at increasing conductivity
- A- and B-site mixing (proven by XRD and NPD) limits effectiveness of dopant
- Counter-doping to prevent defect formation significantly lowers conductivities
- Recent results on pyrochlore-fluorite system shows greater potential for increased conductivity

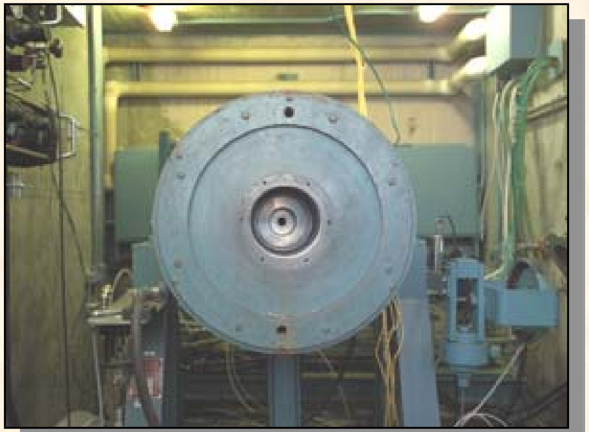
New Low-Temperature Proton Conductor Discovered

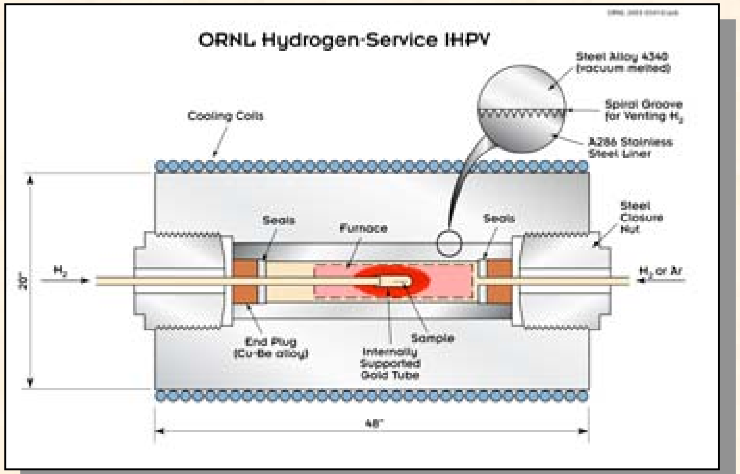


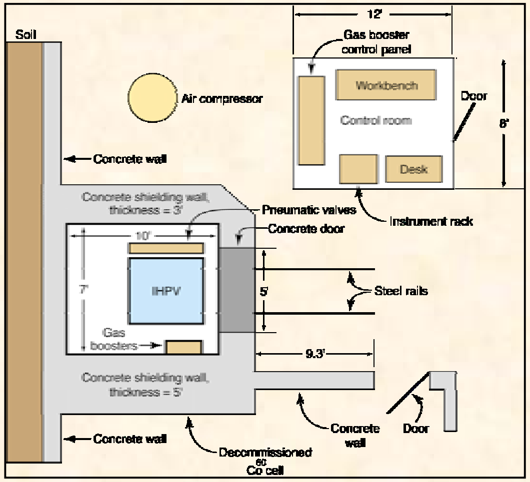


Flux Measurements will be Carried Out in State-of-the-Art Test Facility

- Internally heated pressure vessel
  - Temperature range (20-1000°C)
  - H_2 Pressures (up to 40,000 psi)
  - Fully automated







Interactions and Collaborations

- **Ames Laboratory:** providing novel materials for support tubes
- **Worcester Polytechnic Institute:** discussions ongoing to have WPI deposit Pd membranes on ORNL support tubes
- **NETL:** initial discussions on collaborative effort
- Discussions on implementation of technology are ongoing with
  - **ConocoPhilips, ChevronTexaco, Pall Corp., and Praxair**
- **Rutgers University:** technical collaboration on proton conducting materials

Future Work

- Porous Support Tube Development
  - Continue to identify and characterize materials for support tube fabrication
  - Establish fabrication parameters and fabricate support tubes FY2005
  - Characterize support tubes for strength, permeance, and high temperature stability
  - Expand activity to include composite structure support tubes

- Proton Transport Membranes
  - Continue modeling and simulation effort to predict composition property relationships
  - Determine hydrogen flux as a function of temperature and pressure for candidate compositions
  - Characterize long-term high-temperature stability under service conditions (H_2S, CO_2)
  - Develop metallic supported asymmetric membranes using ORNL support tubes